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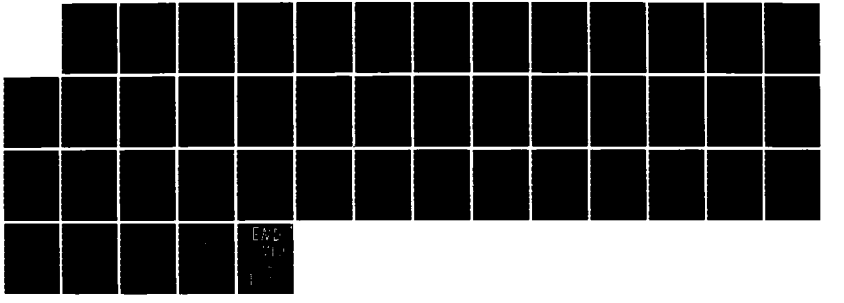

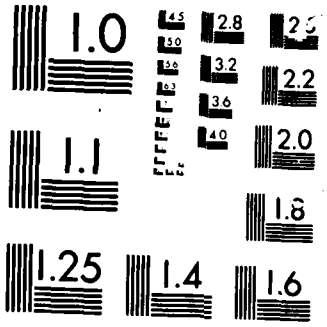

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A MULTIPLE GAUSSIAN WAVE PACKET THEORY OF H_2 DIFFRACTION AND ROTATIONAL EXCITATION BY COLLISION WITH SOLID SURFACES

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A MULTIPLE GAUSSIAN WAVE PACKET THEORY OF H_2 DIFFRACTION AND ROTATIONAL EXCITATION BY COLLISION WITH SOLID SURFACES

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ABSTRACT

We combine Gaussian wave packets and the coupled channel method to develop a theory of H_2 diffraction and rotational excitation by collision with surfaces. This improves our previous work on H_2 diffraction since it eliminates the mean trajectory approximation; it also extends Heller's work to problems in which the dynamics require the creation of new packets which must be coupled to each other as they are propagated through the interaction region. The approximations involved in the above Gaussian wave packet approach can be removed by using extending a method proposed by Fleck, Morris and Feit, which propagates the Gaussian wave function exactly and efficiently.

I. INTRODUCTION

The analysis of various H_2 surface scattering experiments[1-15] requires the use of quantum mechanics in describing the rotational motion and the translation of the center of mass. "Exact" coupled channel calculations are possible only for low incident kinetic energy.[16-18] However, even when feasible, such calculations are tedious and perhaps insufficiently descriptive of the underlying physical processes. As a result much work has been done to develop simpler and hopefully more illuminating approximate procedures.[19-34]

In this paper we present an extension of our previous work[35] in which we used a Gaussian wave packet (GWP) mean trajectory approximation (MTA) method to calculate the diffraction and the rotational excitation of H_2 colliding with a solid surface. The GWP-MTA theory uses a wave function of the form

$$\psi(\vec{R},\theta,\phi;t) = \sum_{\alpha=1}^{N} G_\alpha(\vec{R};t) \sum_{i=1}^{n} c_{\alpha i}(t)\, Y_i(\theta,\phi)\exp\{-i\epsilon_i t/\hbar\}, \tag{I.1}$$

where $\vec{R}$ is the center of mass position and θ and ϕ are the polar and azymuthal angles describing the orientation of the molecular axes in the coordinate system shown in Fig. 1. The functions $Y_i(\theta,\phi)$ are spherical harmonics labelled by the binary index $i = (l,m_l)$, and $G_\alpha(\vec{R},t)$ are Gaussian wave packets. The experimental conditions are such that the vibrational energy of H_2 exceeds all other energies in the system, so we can consider H_2 to be a rigid rotor.

Since we are interested in diffraction we must ensure that the initial state of the center of mass is a plane wave. This is achieved[35-39] by placing the packets G_α, $\alpha=1, \ldots, M$ on a M point square grid which covers the surface unit cell, and by choosing the parameters in each G_α so that for $\vec{R}$ within the unit cell, $\sum_\alpha G_\alpha(\vec{R})$ coincides with the incident plane wave. The translational symmetry of the surface allows us to construct the result of

scattering by the whole surface, from the results of scattering the packets G_α by an unit cell.[35-39]

To explain some of the improvements contained in GWP-MTA we compare it with the customary classical MTA[40-50] (denoted CMTA) which has been applied fairly successfully to surface science problems.[28,29,45] When applied to H_2 scattering CMTA replaces in the Hamiltonian the quantum variable $\vec{R}$ with the "classical" trajectory $\vec{R}(t)$, and uses the wave function $\psi(\theta,\phi) = \Sigma\ c_i(t)\ Y_i(\theta,\phi)\exp\{-i\varepsilon_i t/\hbar\}$. The classical trajectory $\vec{R}(t)$ is obtained by solving Newton's equation with the mean potential $\Sigma\ \Sigma\ c_i^*(t)c_j(t)\ \langle Y_i|V(\vec{R}(t))|Y_j\rangle$ where $V(\vec{R}(t))$ is the surface-molecule interaction energy. By using a classical trajectory MTA eliminates all quantum effects from the motion of the center of mass, except for those contained in the computation of the mean force. The GWP-MTA theory propagates a Gaussian wave packet on the same potential energy as CMTA.[35,50] The use of a wave packet provides a fully quantum mechanical description (albeit a simplified one) of the center of mass motion. The resulting theory describes well such a dramatic quantum effect as diffraction and also gives a good description of the rotational excitation probabilities.[35] Furthermore, GWP-MTA is computationally cheaper than its classical counterpart since the number of GWP's needed to describe the quantum scattering process is substantially smaller than the number of classical trajectories required by CMTA. This can generate substantial savings in computer time since the expense per GWP is roughly twice the expense needed to propagate a classical trajectory. This can be understood metaphorically, by thinking of each packet as a bundle of classical trajectories, which are generated at once by propagating one packet.

Unfortunately GWP-MTA shares with CMTA a shortcoming whose removal is the subject of the present paper. To understand both the origin of this shortcoming as well as its removal by the method proposed here it is useful to compare the GWP-MTA wave function (II.1) with its proposed replacement, which is

$$\psi(\vec{R},\theta,\phi;t) = \sum_{\alpha=1}^{M}\sum_{i=1}^{n} G_{\alpha i}(\vec{R};t)\, Y_i(\theta,\phi)\exp(-i\epsilon_i t/\hbar). \qquad (I.2)$$

The GWP-MTA wave function describes the center of mass motion with one Gaussian per grid point. Superficially this is in agreement with out intuitive belief that a packet represents a localized "corpuscule" (as opposed to a wave) and therefore we must have one trajectory per corpuscule. It is however incorrect to apply this "Newtonian" notion to a system that has discrete internal states (i.e. rotations) which can be excited during collision. This makes the classical motion of the center of mass rather non-Newtonian, since the quantum excitation of the internal motion affects the center of mass motion (at least through the conservation laws). Thus the excitation of an internal state requires the appearance of a new center of mass trajectory whose translational energy is equal to the incident one minus the energy of the internal excitation. Therefore, a correct description of center of mass motion requires one trajectory for each final rotational state. Within the GWP approach this can be achieved by using the wave function (I.2) which has (at each grid point) <u>one packet for each rotational state</u>.

It is now useful to contrast the behavior of the packets in these two theories. The unique packet used in GWP-MTA moves on a mean, rotationally averaged potential surface. A time of flight (TOF) measurement applied to this theory gives <u>one peak</u> in the momentum distribution whose position is determined by the fact that the kinetic energy lost by the center of mass motion equals the total energy taken up by all the rotations; the same TOF measurement on a system described by the multiple GWP theory (MGWP) leads to <u>one peak for each rotational state</u>. In MGWP the post-collision rotational distribution is imprinted in the TOF spectra and with sufficient resolution one could measure the rotational energies by doing TOF measurements. Another way of pointing out differences between the two methods is to examine the results predicted for rotationally selected final state

measurements.[51] GWP-MTA gives the same diffraction spectrum for each rotational state, while MGWP gives different diffraction patterns for each final rotational state. Furthermore for a rotationally selected, angle resolved, TOF measurement GWP-MTA gives the same results for each state Y_i, while MGWP predicts different results for different Y_i.

We emphasize that while the conceptual and qualitative improvements brought about by MGWP method are interesting and necessary, one should not view the use of GWP-MTA with exagerated alarm. The measurements required to discriminate between the two methods are possible but very tedious. Less ambitious (but still difficult) experimental work, such as a measurement of the rotational distribution with a modest angular resolution and without TOF, is likely to be well described by GWP-MTA, since the method of measurement performs experimentally the kind of averaging that GWP-MTA does theoretically. Diffraction measurements with modest angular resolution and no anlysis of the rotational state are also well described by GWP-MTA except for those situations when the angular resolution is sufficient to resolve the diffraction peaks due to molecules that are rotationally excited.[2,6] Such peaks are averaged by the MTA theory together with the rotationally elastic parent peak and will be absent in the predictions of the theory.

Within the existing GWP methodology[52-70] the development of the MGWP scheme requires the solution of several technical problems. The customary propagation scheme assumes that the number of packets is conserved in time, while in the present theory we must start with one packet and emerge with as many packets as many open rotational channels. Thus we must find a method for generating new packets as the incident packet enters the collision zone.

Furthermore, the existing applications of the GWP method to diffraction[36-39] has used what we call the simplest Heller method (SHM), which assumes that the packets can be propagated independently. This assumption cannot be made in the present

problem for the Gaussians $G_{\alpha i}$, i=1, ..., m because the rotational populations are established exclusively through the coupling between the packets having the same α but different i-s. Neglect of this coupling (as in SHM) would suppress rotational excitation from the theory.

The main contribution of the present paper to the GWP technology is the development of a propagation scheme in which Gaussians are created in the process of propagation as needed, and evolve by interacting with each other.

The difficulties encountered by a classical or semi-classical propagation scheme applied to a subset of degrees of freedom which are coupled to a strongly quantum subset, are well known[71-79] and much labor and ingenuity has been devoted to their solution. The present MGWP approach is a new procedure to attack this old problem. Since the space does not permit a detailed comparison between the present and the earlier work,[71-79] we confine ourselves to listing those features that make us hope that the method developed here will be useful. First, the MGWP does not require root searching, classical calculations with double ended boundary conditions, or self-consistent solutions of integro-differential trajectory equations, it is not confined to one dimension, and has no difficulties with the turning points. Second, the GWP equations of motion are almost as simple and sometimes less laborious than the classical ones. The GWP scheme blends easily and naturally with classical mechanics so that quantum scattering calculations from a classically moving lattice are possible.[39] Finally the method lends itself to simple classical like, intuitive interpretation of dynamics.

In the context of surface science GWP methods are relatively new; the existing calculations show that they are reasonably accurate.[35-39] In diffraction problems they can be applied at kinetic energies at which coupled channel calculations are prohibitive. They can be easily used to calculate scattering by disordered surfaces,[37] a problem for which the traditional quantum methods would have extreme difficulties.

The single most important drawback of the GWP method is that it is an "ill-defined" approximation, in the sense that it lacks a precise validity condition, or a convergence scheme which insures the achievement of greater accuracy with increased labor. This cannot be done by increasing the number of packets; in fact it sometimes happens that an increase in the number of Gaussians leads to overcompleteness and worsens the accuracy.[67,69] Practical experience indicates that one should expect good results with little effort for short time dynamical problems involving spatially localized quantum degrees of freedom, which are nearly semi-classical. Recent work by Sawada, Heather, Jackson and Metiu[67] shows that for some problems accurate long time results can also be obtained at the expense of the simplicity of the propagation scheme.

II. THE MULTIPLE GAUSSIANS THEORY OF H_2 SCATTERING

II.1. The Hamiltonian

We use the Hamiltonian

$$H = -(\hbar^2/2M)\nabla^2_{\vec{R}} + (2\mu|r|^2)^{-1}\vec{L}^2 + V(\vec{r}_1,\vec{r}_2) \ , \qquad (II.1)$$

where $\vec{R}$ is the center of mass position, $\vec{r}_1$ and $\vec{r}_2$ are the coordinates of the two atoms forming the diatomic, M=2M and μ=M/2 are the total and the reduced mass of the diatomic, and $\vec{L}$ is the angular momentum operator. The coordinate system is shown in Fig. 1. The interaction energy with the surface is

$$V(\vec{r}_1,\vec{r}_2) = \sum_{i=1}^{2} D_i(\exp[-2\alpha_i(z_i-z_o)]-2\exp[-\alpha_i(z_i-z_o)]) \qquad (II/2)$$
$$-\beta_i D_i \exp[-2\alpha_i(z_i-z_o)][\cos(2\pi x_i/c_1) + \cos(2\pi y_i/c_2)],$$

where c_1 and c_2 are the lattice constants, and $\vec{r}_i \equiv (x_i,y_i,z_i)$. This represents the interaction with a corrugated surface and the forces acting on the molecule depend on both the polar and the azymuthal angle describing the orientation of the molecular axis (Fig. 1). To obtain the equations of motion for the nuclear wave functions $G_{\alpha i}$ we insert the wave function (I.2) in the time dependent Schrodinger equation, use

$$(2\mu|r|^2)^{-1} L^2 Y_i(\theta,\phi) = \epsilon_i Y_i(\theta,\phi) \ , \qquad (II.3)$$

multiply with $Y_j(\theta,\phi)$ sinededϕ, and integrate over angles. This leads to

$$[i\hbar \frac{\partial}{\partial t} + (\hbar^2/2M)\nabla^2_{\vec{R}}]\sum_\alpha G_{\alpha j}(\vec{R};t) = \sum_i V_{ji}(\vec{R})\exp\{-i(\epsilon_j-\epsilon_i)t/\hbar\}(\sum_\alpha G_{\alpha i}).$$

with

$$V_{ji}(\vec{R}) \equiv \int_0^\pi \text{sinede} \int_0^{2\pi} d\phi \ Y_j^*(\theta,\phi)V(\vec{r}_1,\vec{r}_2)Y_i(\theta,\phi) \ . \qquad (II.5)$$

II.2 The Equations of Motion

II.2.A. General Remarks

To use the GWP method for solving the equations (II.4) we assume that $G_{\alpha i}$ are wave packet of the form

$$G_{\alpha i}(\vec{R};t) = \exp[(i/\hbar)((\vec{R}-\vec{R}_{\alpha i}(t))\cdot\overleftrightarrow{A}_{\alpha i}(t)\cdot(\vec{R}-\vec{R}_{\alpha i}(t)) + \vec{P}_{\alpha i}(t)\cdot(\vec{R}-\vec{R}_{\alpha i}) + \gamma_{\alpha i}(t)\}\ . \tag{II.6}$$

Here $\vec{R}_{\alpha i}(t)$ and $\vec{P}_{\alpha i}(t)$ are the expectation values of the position and momentum operators in the state $G_{\alpha i}$, $\overleftrightarrow{A}_{\alpha i}(t)$ is a 3x3 complex matrix which gives the width of the packet and a space dependent phase and $\gamma_{\alpha i}(t)$ is a complex function of time contributing to the phase and the amplitude of the state $G_{\alpha i}$.

The central idea in Heller's work is that the time evolution of the state $G_{\alpha i}$ is given by the evolution of the parameters $\overleftrightarrow{A}_{\alpha i}(t)$, $\vec{R}_{\alpha i}(t)$, $\vec{P}_{\alpha i}(t)$, and $\gamma_{\alpha i}(t)$. In the simplest implementation of this idea (which we call the simplest Heller method (SHM)) it is assumed that: (1) the Gaussians are narrow throughout the collision so that we can expand the potential in the Schrodinger equation (II.4) in power series around the instantaneous position $\vec{R}_{\alpha i}(t)$ of the packet and retain the quadradic part only (the local harmonic approximation (LHA)); and that (2) each Gaussian can be propagated independently (the independent Gaussian approximation (IGA)). The shortcomings of SHM were pointed out in our work[67-69] as well as the work of Skodje and Truhlar[65] and Thirumalai, Bruskin and Berne.[66] Ways of improving SHM, by removing the two approximations presented above were proposed by Sawada, Heather, Jackson and Metiu[67] and by Heller.[52,53]

In this paper we use the minimum error method (MEM)[67] which couples the Gaussians and makes no assumption concerning their width. The only approximation is that $G_{\alpha i}(\vec{R};t)$ maintain their Gaussian form throughout the collision.

Our numerical experience with the coupled Gaussian MEM

theory indicates that the coupling terms vary on a faster time scale than the other terms appearing in the MEM equations. The presence of these terms slows down considerably the integration program and therefore it is desirable to neglect them whenever the penalty is not too severe. In the diffraction calculations carried out by Drohlshagen and Heller[36,37] (for atoms) and by Jackson and Metiu (for atoms[38,39] and diatomics[35]) it was demonstrated that satisfactory results can be obtained if the Gaussians used to construct the incident plane wave are propagated independently. In the present context this suggests that we can assume that $G_{\alpha i}$, $G_{\beta j}$ etc are decoupled when $\alpha \neq \beta$. We cannot however neglect the coupling between the packets $G_{\alpha i}$ i=1, ..., n, since this coupling is the driving force for the rotational excitation of the particle.

II.2.B. The Equations of Motion

To generate the MEM equations of motion for the Gaussian parameters we define[67] the error made by using the Equation (I.2) as:

$$E = \int \left| (\hbar^2/2M)\nabla^2_{\vec{R}} + i\hbar\frac{\partial}{\partial t}) \; G_{\alpha j}(\vec{R};t) - \sum_{i=1}^{n} V_{ij}(\vec{R}) \exp\{i(\epsilon_j - \epsilon_i)t/\hbar\} \right.$$

$$\left. G_{\alpha i}(\vec{R};t) \right|^2 \; d\vec{R} \quad .$$

Since the error made at time t is a function of $\overleftrightarrow{A}_{\alpha i}(t)$, $\vec{R}_{\alpha i}(t)$, $\vec{P}_{\alpha i}(t)$ and $\dot{\gamma}_{ai}(t)$ we determine these quantities so as to minimize the error. This generates first order, non-linear, ordinary differential equations[67] for $\overleftrightarrow{A}_{\alpha i}(t)$, $\vec{R}_{\alpha i}(t)$, $\vec{P}_{\alpha i}(t)$ and $\gamma_{\alpha i}(t)$:

$$\dot{\vec{R}}_{\alpha j}(t) = \frac{1}{M} \vec{P}_{\alpha j}(t) + (\overleftrightarrow{M}^{(2)}_{ij} - Im\overleftrightarrow{A}_{\alpha j}(t))^{-1} Im\vec{F}^{(1)}_{\alpha j} \qquad \text{(II.7a)}$$

$$\dot{\vec{P}}_{\alpha j}(t) = -(\overleftrightarrow{M}^{(2)}_{\alpha j})^{-1} \cdot Re\vec{F}^{(1)}_{\alpha j} + 2Re\overleftrightarrow{A}_{\alpha j}(t)[\dot{\vec{R}}_{\alpha j}(t) - \frac{1}{M} \vec{P}_{\alpha j}(t)]$$

(II.7b)

$$\dot{\overleftrightarrow{A}}_{\alpha j}(t) = \frac{2}{M}\,\overleftrightarrow{A}_{\alpha j}(t)\cdot\overleftrightarrow{A}_{\alpha j}(t) + \overleftrightarrow{S}_{\alpha j} \qquad \text{(II.7c)}$$

and

$$\dot{\gamma}_{\alpha j}(t) = \frac{i\hbar}{M}\,\mathrm{tr}(\overleftrightarrow{A}_{\alpha j}(t)) + \frac{1}{2M}\,\vec{P}_{\alpha j}(t)\cdot\vec{P}_{\alpha j}(t)$$

$$+ \vec{P}_{\alpha j}(t)\cdot[\dot{\vec{R}}_{\alpha j}(t) - \frac{1}{M}\,\vec{P}_{\alpha j}(t)] - \left(\frac{F^{(0)}_{\alpha j}}{(I_{ooo})_{\alpha j}}\right) - \left(\frac{\vec{I}^{(2)}_{\alpha j}\cdot\lambda_{\alpha j}}{(I_{ooo})_{\alpha j}}\right). \qquad \text{(II.7d)}$$

$$F^{(n)}_{\alpha j} = \sum_i \int d\vec{R}(\vec{R}-\vec{R}_{\alpha j}(t))^n\, G^*_{\alpha j}(\vec{R};t)\, G_{\alpha i}(\vec{R};t) V_{ji}(\vec{R}) e^{-i(\epsilon_i-\epsilon_j)t/\hbar} \qquad \text{(II.8)}$$

and

$$\overleftrightarrow{M}^{(2)}_{\alpha j} = \int d\vec{R}(\vec{R}-\vec{R}_{\alpha j}(t)\cdot(\vec{R}-\vec{R}_{\alpha j}(t)|G_{\alpha j}(\vec{R};t)|^2 \,. \qquad \text{(II.9)}$$

Note that $F_{\alpha j}$ is a scalar, $\vec{F}^{(1)}_{\alpha j}$ is a vector with the components

$$(F^{(1)}_{\alpha j})_x \equiv \sum_i \int d\vec{R}(X-X_{\alpha j}(t) G^*_{\alpha j} G_{\alpha i} V_{ji} \exp(i(\epsilon_j-\epsilon_i)t/\hbar), \text{etc.}$$

and $\overleftrightarrow{F}^{(2)}_{\alpha j}$ is a dyadic with the components

$$(F^{(2)}_{\alpha j})_{xy} \equiv \sum_i \int d\vec{R}(X-X_{\alpha j}(t))(Y-Y_{\alpha j}(t))$$

$$G^*_{\alpha j}\, G_{\alpha i} V_{ji} \exp(-i(\epsilon_j-\epsilon_i)t/\hbar), \text{ etc.}.$$

The complex matrix $\overleftrightarrow{S}_{\alpha j}$ and the vectors $\vec{I}_{\alpha j}$ and $\vec{\lambda}_{\alpha j}$ are defined in the Appendix, where we also give an outline of the derivation of the equations presented above.

II.3 The Choice of Initial Condition

In order to solve the equations (II.7) we must choose initial values for the parameters $\overleftrightarrow{A}_{\alpha i}(0)$, $\vec{R}_{\alpha i}(0)$, $\vec{P}_{\alpha i}(0)$, $\gamma_{\alpha i}(0)$. As discussed often in literature the GWP method does not provide an unique and fully justifiable method for specifying these values. However in the particular case of atom or diatom diffraction, prescriptions that work well have been proposed and we see no reason to modify them.[35-39] Thus if the initial rotational state is Y_i we take $G_{\alpha j}=0$ for $j\neq i$ and define the parameters of $G_{\alpha i}$ such that $\sum_\alpha G_{\alpha i}(\vec{R};0)$ is a plane wave when $\vec{R}$ takes values within the unit cell of the solid surface. The way to do this was discussed in several papers.[35-39]

While this provides initial conditions for the equations propagating the parameters in $G_{\alpha i}$, it says nothing about the initial conditions for $G_{\alpha j}$, $j\neq i$. There is a physical reason for this: the initial state $\sum_\alpha G_{\alpha i}$ is prepared by the experimentalist, while $\Sigma\, G_{\alpha j}$ is generated by the collision process. The available GWP procedures have no provisions for the birth of new packets. To circumvent this difficulty we propose the procedure described below.

We consider the case in which the incident molecules are in state Y_k and the incident state of the center of mass is constructed with the packets $G_{\alpha k}$, $\alpha=1, \ldots, M$. Let us denote by t_o the last time when we can still assume that the packets $G_{\alpha l}$, $l\neq k$ have zero amplitude. At that time the packets satisfy the equations

$$\left(i\hbar \frac{\partial}{\partial t} + (\hbar^2/2M)\nabla_R^2\right) G_{\alpha k}(\vec{R};t) = V_{kk}(\vec{R})G_{\alpha k}(\vec{R};t) \qquad \text{(II.10a)}$$

and

$$\left(i\hbar \frac{\partial}{\partial t} + (\hbar^2/2M)\nabla_{\vec{R}}^2\right)G_{\alpha l}(\vec{R};t) = V_{lk}(\vec{R})\exp\{-i(\epsilon_k-\epsilon_l)t/\hbar\}G_{\alpha k}(\vec{R};t)$$

$$l\neq k,\ l=1,2,\ldots,m \qquad \text{(II.10b)}$$

According to these equations a new packet $G_{\alpha l}(\vec{R};t)$ is generated

when the initial packet $G_{\alpha k}(\vec{R};t)$ starts overlapping with $V_{lk}(\vec{R})$.

To create the new packet $G_{\alpha l}(\vec{R};t_o+\tau)$ we solve Eq(II.10b) for a short time τ. This gives

$$G_{\alpha l}(\vec{R};t_o+\tau) = -(i\tau/\hbar)(M/i\hbar 2\pi\tau)^{3/2} \int_{-\infty}^{+\infty} d\vec{R}'$$

$$\exp\{(i/\hbar)[(M/2\tau)(\vec{R}-\vec{R}')^2]\ V_{lk}(\vec{R}')G_k(\vec{R}';t_o)$$

$$\exp\{-(i/\hbar)(\epsilon_k-\epsilon_l)t_o\}\ . \qquad \text{(II.11)}$$

A rather tedious calculation shows that for the surface-molecule potential (II.2) the quantity $V_{lk}(\vec{R}')$, defined by Eq. (II.5), is a Gaussian. Therefore the integrand in Eq. (II.11) is a product of Gaussians and therefore the integration gives a Gaussian for $G_{\alpha l}$. If $V_{lk}(\vec{R}')$ has a complicated non-Gaussian form the integral can be very accurately performed (since τ is arbitrarily small) by using the stationary phase approximation and this also gives a Gaussian result.

It should be noted that the above procedure is nothing else but perturbation theory with respect to τV_{lk} followed by an asymptotic evaluation of an integral by using the fact that the inverse length $(M/2\tau\hbar)^{1/2}$ is very large compared to all other length scales in the problem (i.e. the width of $G_{\alpha k}$ and the length scale over which $V_{lk}(\vec{R})$ changes). Because we control the magnitude of τ this procedure is essentially exact.

Our numerical experience with charge transfer problems[80] shows that it is possible to generate all packets at once, even if for some of them the term $V_{mk}G_{\alpha k}$ is very small due to poor overlap. The outcome is that the new packet $G_{\alpha m}$ has a much smaller initial amplitude than the other new packets, as it should. Subsequent propagation will increase that amplitude as $V_{mi}G_{\alpha i}$ increases.

A serious danger in using such a method is that the results may depend on the moment t_o chosen for new packet generation. There is some numerical experience regarding this possibility,

which indicates that the results are remarkably stable with respect to this choice.[80]

II.4 A Simplified Model and A Qualitative Discussion of the Theory

The notation used so far gives a compact representation of the equations of motion (II.7) for the Gaussian parameters, but obscures to some extent their physical meaning. In this Section we discuss a limiting case which is designed to simplify the computational scheme and bring out its physical content. The approximations made are sufficiently reasonable to give us hope that the simplified scheme might also be accurate enough to be computationally useful.

As Heller pointed out, in the simplest version of his method (SHM) $\vec{R}(t)$ and $\vec{P}(t)$) follow classical equations of motion and the phase $Re\gamma(t)$ is essentially the classical action. These results are obtained only if the Gaussians are narrow (LHA) and decoupled (IGA).

The MEM version of the theory[67] does not make these simplifying assumptions and as a result loses the simple features mentioned above. Nevertheless, it is still useful to think of the equation of motion for $\vec{R}_{\alpha i}$ and $\vec{P}_{\alpha i}$ as evolving according to a mechanics which is similar to, but more complicated than the classical one; for lack of a better term we call this a corpuscular mechanics (we have also used in our work the term pseudo-classical). When the MEM theory uses only one packet $G_{\alpha i}$ the force acting on the center of the packet is not $-\partial V_i(R_{\alpha i})/\partial R_{\alpha i}$ (as in the simple Heller method) but $-\partial/\partial\vec{R}_{\alpha i} \int G^*_{\alpha i} V_i G_{\alpha i} d\vec{R}$. Since the quantity $|G_{\alpha i}|^2$ appearing in this integral depends on $ImA(t)$, the above force depends on time and the motion of the center of the packet is not conservative. Various interesting features of this potential and the resulting "corpuscular mechanics" were discussed and exemplified by Heather and Metiu.[68] The use of several coupled Gaussians further complicates the picture since the motion of their centers is now coupled through terms that have no classical analog and which are turned on by the overlap between

the packets (i.e. they depend on the quantity $\int d\vec{R}(\vec{R}-\vec{R}_i)$ $G_i^* G_j V_{ij}(R)$).

In what follows we analyze the meaning of the MEM equations (II.7) by making some of the approximations used by the SHM.[67-69] First we emphasize again that while in previous applications of MEM we coupled the Gaussians in order to increase the accuracy of the calculations, in the present work the coupling between the Gaussians $G_{\alpha i}$, i=1,...,n with the same α is essential on physical grounds. It is this coupling that allows the amplitudes of various Gaussians to vary and give us the final rotational distribution. The probability that a particle is in the rotational state Y_i is proportional to $\int d\vec{R} \sum_{\alpha} G^*_{\alpha i} G_{\alpha i}$ which depends on $\mathrm{Im}\gamma_{\alpha i}(t)$ and $\det(\mathrm{Im}\overleftrightarrow{A}_{\alpha i}(t))$. Thus to compute this probability correctly it is essential that the coupling between the Gaussians $G_{\alpha i}$, i=1, ..., n is present in the equation of motion for $\gamma_{\alpha i}(t)$ and $\overleftrightarrow{A}_{\alpha i}(t)$; however, we might expect that the coupling may be neglected, without causing a dramatic qualitative deterioration of the results, in the equations of motion for $\vec{R}_{\alpha i}$ and $\vec{P}_{\alpha i}$.

If we begin with the Equation (II.7a) for $\vec{R}_{\alpha j}$ we find that the coupling between packets enters through $\mathrm{Im}\,\vec{F}^{\Delta S}_{\alpha j}$. This quantity can be written as (see Eq. (II.9)).

$$\mathrm{Im}\vec{F}^{(1)}_{\alpha j} \equiv \sum_i \mathrm{Im}\vec{f}_{ij} \qquad \text{(II.12)}$$

with

$$\vec{f}_{ij} = \int d\vec{R}(\vec{R}-\vec{R}_{\alpha j}(t)) G^*_{\alpha j}(R;t) V_{ji}(\vec{R}) G_{\alpha i}(\vec{R};t) \exp(-i(\epsilon_i-\epsilon_j)t/\hbar) \qquad \text{(II.13)}$$

The diagonal term $\vec{f}_{jj}(t)$ is real and therefore does not contribute to $\mathrm{Im}\,\vec{F}_{\alpha j}$. We are thus left with the off-diagonal terms $\vec{f}_{ij}$, $i\neq j$, only. These represent the effect of the coupling of $G_{\alpha j}$ to the other Gaussians $G_{\alpha i}$, $i\neq j$. Since we argued that in the equation for $\vec{R}_{\alpha j}$ this coupling is not physically essential we neglect it, and therefore can take $\vec{F}^{(1)}_j \simeq 0$.

This assumption is also reasonable in view of our past experience with coupled Gaussian calculations. We have found that the time evolution of the terms $G^*_{\alpha i}G_{\alpha j}$ is much more rapid than that of $|\vec{R}_{\alpha i}|^2$ or $|\vec{R}_{\alpha j}|^2$ because of rapid changes in the difference between the phases of $G^*_{\alpha i}$ and $G_{\alpha j}$. Thus the terms $\vec{f}_{ij}, i\neq j$, oscillate very rapidly and their effect on the evolution of $\vec{R}_{\alpha j}$ may average to zero when the equation of motion for $\vec{R}_{\alpha j}$ is integrated; furthermore the phase $\exp\{i(\epsilon_i-\epsilon_j)t/\hbar\}$ can play the same role. Moreover $\vec{f}_{ij}$ is non-zero only when $G^*_{\alpha i}$, V_{ij} and $G_{\alpha j}$ overlap which means that $\vec{f}_{ij}$ is practically zero at least at some times during collision.

If these arguments are accepted we can replace (II.7a) with

$$\dot{\vec{R}}_{\alpha j} \simeq \vec{P}_{\alpha j}/M \qquad \text{(II.14)}$$

which implies that the center of each packet $G_{\alpha j}$ moves like a classical particle with momentum $\vec{P}_{\alpha j}$.

A similar discussion can be made to simplify Eq.(II.7b) (giving the evolution of $\vec{P}_{\alpha i}$) by neglecting $\vec{f}_{ij}$ when $i\neq j$. The use of Eq. (II.14) in (II.7b) removes the last term in the latter equation. If we further assume that the Gaussian $G_{\alpha j}$ is narrow throughout collision we can expand $V_{jj}(\vec{R})$ appearing in the integrand of $\vec{f}_{jj}$ (see Eq. (II.13)) and obtain

$$\vec{f}_{jj} \simeq \int d\vec{R}\ (\vec{R}-\vec{R}_{\alpha j}(t))(\vec{R}-\vec{R}_{\alpha j}(t))|G_{\alpha j}(R;t)\cdot\frac{\partial V_{jj}(\vec{R}_{\alpha j}(t))}{\partial \vec{R}_{\alpha j}(t)}$$

$$\simeq \overleftrightarrow{M}^{(2)}_{\alpha j}\cdot\partial V_{jj}(\vec{R}_{\alpha j}(t))/\partial\vec{R}_{\alpha j}(t).$$

The last term follows from Eq. (II.9). Using these approximations and Eq. (II.12) in Eq. (II.7.b) leads to

$$\dot{\vec{P}}_{\alpha j}(t) = -\partial V(\vec{R}_{\alpha j}(t))/\partial\vec{R}_{\alpha j}(t). \qquad \text{(II.15a)}$$

If we don't assume a narrow Gaussian we have

$$\dot{\vec{P}}_{\alpha j}(t) = -[\overleftrightarrow{M}_{\alpha j}^{(2)}(t)]^{-1}\cdot\vec{f}_{jj}(t)$$

$$= -[\overleftrightarrow{M}_{\alpha j}^{(2)}(t)]^{-1}\cdot\int d\vec{R}(\vec{R}-\vec{R}_{\alpha j})V_{jj}(R)|G_{\alpha j}(\vec{R};t)|^2 \qquad \text{(II.15b)}$$

Thus the use of the independent Gaussians approximation (IGA) in (II.7a) and (II.7b) leads to (II.14) and (II.15b); the additional assumption that the potential energy is locally harmonic (LHA) simplifies (II.15b) and gives (II.15a). If both LHA and IGA are used each packet center moves classically on the potential $V_{jj}(\vec{R}_{\alpha j}(t))$, which is the expectation value of the molecule surface potential energy when the molecule is in the rotational state Y_j. If LHA is abandoned the motion resembles superficially the classical one. However the force $-[\overleftrightarrow{M}_{\alpha j}^{(2)}]^{-1}\cdot\vec{f}_{jj}$ is time dependent and the motion of the packet is non-conservative. As shown by Heather and Metiu[68,69] this is a necessary feature which ensures the conservation of energy; if LHA and IGA are used the "classical energy" $\vec{P}_{\alpha j}^2/2M + V(\vec{R}_{\alpha j}(t))$ is conserved, but the quantum one isn't.

We emphasize that the use of IGA to decouple the motion of the centers of the packets is not likely to lead to qualitative errors for short collision times, and simplifies considerably the propagation scheme through the elimination of the rapidly varying coupling terms. There is, as yet, no proof that the errors made by using these simplified equations are small and the usefulness of these equations remains to be tested. In support of this simplified theory we note that it is superior to all classical trajectory methods which use one trajectory only since it has, as is conceptually required, one trajectory for each rotational state. On conceptual grounds the theory also compares favorably with the well known Preston-Tully (PT) method,[75] while being less demanding numerically. Like PT we have multiple trajectories, one for each rotationally averaged energy surface. Unlike PT the GWP procedure - even in its simplest form discussed in this Section- describes the center of mass motion by using a nuclear wave

function. The trajectories are only a simplifying device for propagating these wave functions. As a result the present theory uses probability amplitudes while PT attaches to each state a probability, ignoring the superposition principle and losing interference effect. Thus, the present theory describes interference dominated phenomena - such as diffraction - rather well while PT cannot describe them at all. Furthermore the use of GWP's (with (II.15b)) maintains Heisenberg principle in the theory and this should improve the dynamics, especially if zero point motion is important. Finally we compute observables describing center of mass motion by using the rules of quantum mechanics (i.e. wave functions, operators, matrix elements, etc.) while the PT method is confined to classical rules. Thus, for example, all effects of quantum fluctuations (e.g. the fact that $\langle G|\hat{P}^2|G \neq \langle G|\hat{P}|G\rangle^2$) are lost in the PT method. Nevertheless while conceptual improvements are pleasing, a direct numerical comparison between MGWP and PT is required to test whether such improvements have any practically useful consequences.

III. DISCUSSION

III.1 Remarks regarding the errors made by MGWP

The errors in MGWP are made because (1) we propagate the packets originating from different grid points independently and (2) we force them to maintain their Gaussian form throughout the collision.

The statement that it is erroneous to propagate $\psi = \Sigma\, G_\alpha$ by propagating each G_α independently seems to be at odds with the linearity of Schrodinger equation. Indeed if we apply to $\psi(0) = \Sigma\, G_\alpha(0)$ the exact propagator $U(t)$ to calculate

$$\psi(t) = U(t)\psi(0) = \sum_\alpha U(t)G_\alpha \,, \qquad \text{(III.1)}$$

it automatically follows that

$$\langle\psi(t)|\hat{A}|\psi(t)\rangle = \sum_{\alpha,\beta} \langle G_\alpha(0)|U(t)^\dagger \hat{A} U(t)|G_\beta(0)\rangle \qquad \text{(III.2)}$$

for any operator $\hat{A}$. If we take $\hat{A}=1$ and if $U(t)^\dagger = U(t)^{-1}$, the propagation scheme will conserve the norm; if $\hat{A}=H$ and $U(t)H=HU(t)$ the conservation of energy follows. These conclusions hold even if $U(t)$ is approximate, as long as it is unitary and commutes with the Hamiltonian.

However the application of the GWP method with independent Gaussians to several (but not all) examples[67] shows that the above conservation does not hold; moreover, if the Gaussians are coupled, the conservation properties are restored.

This discrepancy between the conclusions of the familiar analysis presented above and the numerical calculation is due to the peculair nature of the GWP propagation method which calculates $U(t)G_\alpha(0)$ by separately optimizing $U(t)$ for each packet G_α. Thus the result of such a calculation is more properly denoted $U_\alpha(t)G_\alpha$. As long as it is applied to G_α the GWP propagator is unitary (i.e. conserves the norm $\langle G_\alpha(0)|G_\alpha(0)\rangle$) and commutes with the Hamiltonian (i.e. $\langle G_\alpha(0)|H|G_\alpha(0)\rangle$ is conserved). There is

however no assurance that $U_\alpha(t)^+ U_\beta(t) G_\beta = G_\beta$ nor that $U_\alpha H G_\beta = H U_\alpha G_\beta$. Because of this, the quantity

$$\langle\psi(t)|\hat{A}|\psi(t)\rangle = \sum_\alpha \sum_\beta \langle G_\alpha(0)|U_\alpha(t)^\dagger \, O U_\beta(t)|G_\beta(0)\rangle \ , \quad \text{(III.3)}$$

is not conserved for $\hat{A}=1$ or for $\hat{A}=H$. The MEM procedure does not have this shortcoming since it seeks an optimum propagator for the whole sum $\Sigma\, G_\alpha$ rather than for each G_α independently, and therefore (III.2) and its consequences are valid.

The use of the IGA in developing the MGWP procedure is based on its success in previous diffraction calculations. We have no detailed understanding of the reasons for this success, other than the qualitative argument that the IGA-GWP approximation gives each packet a phase that is very similar to that given by the semi-classical theory,[81] which is known to work well for diffraction.[82-85] Nevertheless it is of interest to discuss a computational method which removes the IGA approximation as well as the restriction that the packets maintain their Gaussian form during collision. This is based on ideas advanced by Fleck, Morris, and Feit[86] (FMF) (summarized in Section III.2) applied to the MGWP theory of H_2 scattering (Section III.3).

III.2 A brief description of FMF method

The starting point of the FMF method is similar to that used in path integral theory. The long time propagator U(T) is written as

$$W(T) \simeq U(\tau)^n \qquad \text{(III.4)}$$

with $n\tau=T$. The short time propagator $U(\tau)$ has the "split" form

$$U(\tau)=\exp\{(i\tau\hbar^2/4M)\nabla^2_{\vec{R}}\}\exp\{-i\tau V(\vec{R})\}\exp\{(i\tau\hbar^2/4M)\nabla^2_{\vec{R}}\} \qquad \text{(III.5)}$$

It is easy to see that U(T) can also be written as

$$U(T)=\exp\{(i\tau\hbar^2/4M)\nabla^2_{\vec{R}}\}\exp\{-i\tau V(\vec{R})\}W(\tau)^{n-2}\exp\{i\tau\hbar^2/4M)\nabla^2_{\vec{R}}\}, \qquad \text{(III.5)}$$

where

$$W(\tau) \equiv \exp\{(i\tau\hbar^2/2M)\nabla^2_{\vec{R}}\}\ \exp\{-i\tau V(\vec{R})\} \qquad \text{(III.6)}$$

is the more familiar expression for the short time propagator appearing in the discrete form of the path integral formula for U(T). The error made by using (III.5) is of order τ^3, for each time step τ, while the discrete path integral formula $U(T) = W(\tau)^n$ makes an error of order τ^2 at each time step.

To explain the FMF algorithm we examine the computation of the elementary step $W(\tau)|\psi(t)>$. Using (III.6) and straightforward manipulations based on the representation theory we can write

$$\langle\vec{R}'_\mu|\psi(t+\tau)\rangle \equiv \langle\vec{R}'_\mu|W(\tau)|\psi(t)\rangle =$$

$$= \langle\vec{R}'_\mu|\vec{k}_\nu\rangle\exp\{-(i\tau\hbar^2\vec{k}^2_\nu/2M)\}\langle\vec{k}_\nu|\vec{R}_\eta\rangle\exp\{-i\tau V(\vec{R}_\eta)\}$$

$$\langle\vec{R}_\eta|\psi(t)\rangle \ . \qquad \text{(III.7)}$$

Here we have discretized the variables $\vec{k}$ and $\vec{R}$ and used the rule that repeated variables are summed over. In the customary path

integral theory the integral over $\vec{k}_\nu$ is done analitically and generates the familiar Gaussian $A_{\mu\eta} = (2\pi i\tau/M)^{-1/2} \exp\{im(\vec{R}_\mu-\vec{R}_\eta)^2/2\hbar\tau\}$. We are thus left with only one integral, over $\vec{R}_\eta$ which must be performed numerically. This amounts to a multiplication by the diagonal matrix $B_{\eta\mu}=\delta_{\eta\mu}\exp\{-i\tau V(\vec{R}_\eta)\}$, followed by multiplication with the matrix $A_{\mu\eta}$. If a proper discrete representation of the function $\exp\{-iV(\vec{R})\}\langle\vec{R}|\psi\rangle$ requires a grid having N^d points (d is the dimension of the vector $\vec{R}$) the calculation outlined above requires $N^{2d} + N^d$ operations per time step. This kind of calculation has been performed by Thirumalai and Bruskin Berne[87] who used it to evaluate the path integral formula for the partition function, which is the imaginary time verison of our problem.[88]

The FMF method does perform both integrals in (III.7) (i.e. the sums over $\vec{k}_\nu$ and $\vec{R}_M$) numerically. At first this seems to be a rather bad idea since it should be more expensive to double the number of integrals. However this is not the case. Since $\langle\vec{k}_\nu|\vec{R}_\eta\rangle = (2\pi)^{-3/2} \exp\{-i\vec{k}_\nu\cdot\vec{R}_\eta\}$ both integrals in (III.7) are Fourier transforms and the use of a fast Fourier transform (FFT) algorithm requires only $(N \ln N)^d$ operations for each integral. Thus, this leads to a much faster algorithm than the evaluation of the path integral by the matrix multiplication procedure. The additional efficiency comes from both the use of the split propagator formula, (III.5) which reduces the number of time steps, and the use of FFT which reduces the number of operations per time step. The method can be applied equally well for real time or imaginary time problems.[89] We emphasize however that the rapid growth of labor with dimensionality confines this method to a small number (≤ 4) of quantum degrees of freedom; for imaginary time calculations on systems with higher dimensionality Monte Carlo methods should be vastly superior; for real time problems the Monte Carlo procedure still has severe difficulties which take it out of contention.

The relationship between FMF and the coupled channel method (CC) depends on the problem considered and should be examined with some care, since a kind of complementarity exists between them.

For strongly quantum degrees of freedom (i.e. those whose excitation energy is of the order of the collision energy) the CC method is very efficient since it requires a small basis set. For weakly quantum variables, however, CC is very inefficient. The FMF on the other hand is less sensitive to the number of open states for each degree of freedom, and depends mostly on the extent of their localization. Localized states interacting through localized potentials requires small grids for discretizing $\exp\{-i\tau V(\vec{R})\}\langle\vec{R}|\psi\rangle$; in such cases N is small and FMF is very efficient. At this point it should be apparent why the use of Gaussian wave packets to describe translational motion would combine very well with a FMF propagation scheme: (a) the initial Gaussian packet is spatially localized and this makes FMF efficient; (b) for reasonably brief collisions the packet may evolve into a non-Gaussian wave function but it is likely to stay spatially localized; (c) the use of a GWP initial state is not a limitation since the analysis of the resulting asymptotic state easily yields the S matrix between many incoming and outgoing plane waves; (d) if an incident wave function $\psi(x)$ is spatially extended we can break it up in a sum of pieces (i.e. we can write $\psi(x;0) = \Sigma\ \phi_\alpha(x;0)$ where ϕ_α can be GWP's, for example) each having a smaller support and thus requiring a smaller grid. Since FMF is exact each piece can be propagated independently and the scattered wave function can be exactly rebuilt as the coherent sum of the scattered pieces. In principle this procedure is ideally suited for parallel computing.

For internal degrees of freedom-which are localized by definition-the FMF is almost always convenient. Our calculations of the evolution of the Morse ground state driven by a laser show it to be extremely efficient.[90]

Another great advantage of the FMF method is that it only requires the values of the potential at grid points. We do not need to compute matrix elements between the potential and a basis set as in CC, and the complexities associated with chosing potential forms and basis sets which are compatible (i.e. lead to

integrals that are easy to compute) does not appear. This is particularly important when the quantum system interacts with a classical many body system and the potential is generated numerically by a Monte Carlo or molecular dynamics procedure.

III. The application of FMF to the MGWP theory of H_2 Scattering

As in the case of the GWP approach to this problem it is convenient to use the hybrid coupled channel - GWP approach embodied in the wave function (I.2). Since FMF is exact the decoupling of $G_{\alpha i}$, $G_{\beta j}$ for $\alpha \neq \beta$ is no longer an approximation; furthermore the wave functions $G_{\alpha i}$ start by being Gaussians but are allowed to take any form imposed by the dynamics. Thus all the approximations made by MGWP are removed.

Since we use the wave function (I.2) we must solve the wave equation (II.5). For each α the wave function is an m-dimensional vector $\phi_\alpha(\vec{R};t) \equiv (G_{\alpha i}(\vec{R};t), \ldots, G_{\alpha m}(\vec{R};t))$, where $G_{\alpha i}$ is Gaussian at time t=0 only. The potential energy $V_{ij}(\vec{R})$ is a mxm matrix. To compute the quantity

$$\exp\{i\tau V(\vec{R}_\eta)\} \cdot \phi_\alpha(\vec{R}_\eta;t) \qquad \text{(III.8)}$$

required in (III.7) we must diagonalize the matrix $\overleftrightarrow{V}(\vec{R}_\eta)$ for every grid point $\vec{R}_\eta$. This must be done only once at the beginning of the iteration scheme. If we denote by $\overleftrightarrow{\Lambda}(\vec{R}_\eta)$ the diagonal matrix having the elements $\Lambda(\vec{R}_\eta)_{ij} = \exp\{-i\tau\lambda_i(\vec{R}_\eta)\}\delta_{ij}$, where $\lambda_i(\vec{R}_\eta)$ is an eigenvalue of $\overleftrightarrow{V}(\vec{R}_\eta)$, then we can write

$$\overleftrightarrow{B} \equiv \exp\{-i\tau\ \overleftrightarrow{V}(\vec{R}_\eta)\} = \overleftrightarrow{U}(\vec{R}_\eta)\overleftrightarrow{\Lambda}(\vec{R}_\eta)\overleftrightarrow{U}(\vec{R}_\eta)^{-1}. \qquad \text{(III.9)}$$

Applying the matrix $\overleftrightarrow{B}$ to ϕ gives

$$f_i(\vec{R}) = B_{ij}(\vec{R})\ \phi_{\alpha j}(\vec{R}). \qquad \text{(III.10)}$$

Equation (III.7) requires us to Fourier transform each $f_i(\vec{R})$ separately. When this is done we obtain

$$F_i(\vec{k}_\nu) = \sum_{\vec{R}_\eta} \langle \vec{k}_\nu \mid \vec{R}_\eta \rangle f_i(\vec{R}_\eta) \quad . \qquad \text{(III.11)}$$

The multiplication of ϕ with A requires m^2 steps per grid point $\vec{R}_\alpha$ and $N^d m^2$ steps for the whole grid. The FFT leading to (III.11) requires $(N \ln N)^d m$ operations.

To complete the time propagation, for one time step, we must perform

$$\sum_{\vec{k}_\nu} \langle \vec{R}'_\mu | \vec{k}_\nu \rangle \exp(-i\tau\hbar^2\vec{k}_\nu^2/2M) F_i(\vec{k}_\nu) \qquad \text{(III.12)}$$

and this requires $(N \ln N)^d m$ operations. The total is $N^d m^2 + 2M (N \ln N)^d$ per time step. Of course we must multiply this with the number of time steps n and the number p of packets G_α required to construct the original wave function; the total number of operations is $Pn\{N^d m^2 + 2m(N \ln N)^d\}$; this formula indicates that this calculation is feasible on a fast computer.

It is interesting to note the possibility that a calculation in which we take too few time steps and too coarse a spatial grid might have some value since these approximations cut off the fast excitations (i.e. those transitions having high frequencies) and the high momentum components of the wave function. It is conceivable that this happens without strong distorsion of the lower and mid frequency and momentum part of the wave function. Our experimentations with simple models[90] confirms this assumption, but of course it does not imply that this must a general property.

We note that it might appear that a scattering calculation require a large grid since the FFT subroutine is such that the wave function is reflected by the grid boundary. Thus it appears that we must place the grid edge very far from the scattering center, to permit the wave function to escape completely from the interaction region without reaching the border of the grid. One can avoid this by removing pieces of the wave function as soon as

they emerge from the interaction region and before they reach the grid.[90] Then the total scattered wave function can be reconstructed from these pieces with very little effort.[90]

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FIGURE CAPTIONS

Fig. 1. The coordinate system used in this paper XYZO is fixed, with the XOY plane on the surface and the OZ axes pointing towards the vacuum, and describes the position of the center of mass of the diatomic AB. The axis of the system XYZ are parallel to those of XYZ, and the center of the coordinate system is moving with the center of mass of the molecule. θ and ϕ describe the onculation of the molecule with respect to the surface. The interatomic distance is frozen.

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APPENDIX

To derive equations of motion for the parameters $\overleftrightarrow{A}_{\alpha i}$, $\vec{R}_{\alpha i}$, $\vec{P}_{\alpha i}$ and $\gamma_{\alpha i}$ appearing in each Gaussian wave packet we start from the expression for the error E given in the text above the Equation (II.7a). We introduce in the formula for E the Eq. (II.6) for $G_{\alpha i}$ and take the time derivatives indicated in E. This leads to a bilinear expression in $\overleftrightarrow{A}_{\alpha i}$, $\dot{\vec{R}}_{\alpha i}$, $\dot{\vec{P}}_{\alpha i}$ and $\dot{\gamma}_{\alpha i}$. Minimizing E with respect to the above variables (i.e. $\dot{\overleftrightarrow{A}}_{\alpha i}$, $\dot{\vec{R}}_{\alpha i}$, etc.) leads to

$$\int d\vec{R}(\vec{R}-\vec{R}_{\alpha j}(t))^n\, G^*_{\alpha j}(\vec{R};t)\Big[\Big(\frac{\hbar^2}{2\mu}\nabla_R^2 + i\hbar\frac{\partial}{\partial t}\Big) G_{\alpha j}(\vec{R};t) - \sum_i G_{\alpha i}(\vec{R};t)V_{ji}(\vec{R})e^{-i(\epsilon_i-\epsilon_j)t/\hbar}\Big] = 0 \quad ,$$

where n = 0,1, and 2. The resulting three equations can be written as

$$\int d\vec{R}\Big((\vec{R}-\vec{R}_{\alpha j}(t))\cdot\Big[\dot{\overleftrightarrow{A}}_{\alpha j}(t) + \frac{2}{M}\overleftrightarrow{A}_{\alpha j}(t)\cdot\overleftrightarrow{A}_{\alpha j}(t)\Big]\cdot(\vec{R}-\vec{R}_{\alpha j}(t)) \qquad (A.1)$$
$$|G_{\alpha j}(\vec{R};t)|^2\Big) + (I_{ooo})_{\alpha j}B_{\alpha j}(t) + F^{(0)}_{\alpha j} = 0$$

$$\overleftrightarrow{M}^{(2)}_{\alpha j}\cdot\Big[\dot{\vec{P}}_{\alpha j}(t) + 2\Big(\frac{1}{M}\vec{P}_{\alpha j}(t) - \dot{\vec{R}}_{\alpha j}(t)\cdot\overleftrightarrow{A}_{\alpha j}(t)\Big] + \vec{F}^{(1)}_{\alpha j} = 0 \qquad (A.2)$$

$$\int d\vec{R}\Big((\vec{R}-\vec{R}_{\alpha j}(t))^2\Big[(\vec{R}-\vec{R}_{\alpha j}(t))\cdot\Big(\dot{\overleftrightarrow{A}}_{\alpha j}(t) + \frac{2}{M}\overleftrightarrow{A}_{\alpha j}(t)\cdot\overleftrightarrow{A}_{\alpha j}(t)\Big) \qquad (A.3)$$
$$(\vec{R}-\vec{R}_{\alpha j}(t))\Big]\cdot|G_{\alpha j}(\vec{R};t)|^2\Big) + \overleftrightarrow{M}^{(2)}_{\alpha j}B_{\alpha j}(t) + \overleftrightarrow{F}^{(2)}_{\alpha j} = 0.$$

where

$$B_{\alpha j}(t) = -\frac{i\hbar}{M}\,\mathrm{tr}(\overleftrightarrow{A}_{\alpha j}(t)) + \dot{\gamma}_{\alpha j}(t) + \frac{1}{2M}\,\vec{P}_{\alpha j}(t)\cdot\vec{P}_{\alpha j}(t) - \vec{P}_{\alpha j}(t)\cdot\dot{\vec{R}}_{\alpha j}(t)$$

$$(I_{nlm})_{\alpha j} = \int d\vec{R}\,(X-X_{\alpha j}(t))^n (y-y_{\alpha j}(t))^l (Z-Z_{\alpha j}(t))^m |G_{\alpha j}(\vec{R};t)|^2,$$

$$F^{(n)}_{\alpha j} = \sum_i \int d\vec{R}\,(\vec{R}-\vec{R}_{\alpha j}(t))^n\, G^*_{\alpha j}(\vec{R};t) G_{\alpha i}(\vec{R};t) V_{ji}(\vec{R}) e^{-i(\epsilon_i-\epsilon_j)t/\hbar} \qquad (A.4)$$

and

$$\overleftrightarrow{M}^{(2)}_{\alpha j} = \int d\vec{R}\,(\vec{R}-\vec{R}_{\alpha j}(t))^2 |G_{\alpha j}(\vec{R};t)|^2 \quad . \qquad (A.5)$$

The equations (A.1-3) represent 13 complex equations, although (A.3) is symmetric. $F^{(o)}_{\alpha j}$ is a sum of matrix elements coupling the state j to other rotational states. $\vec{F}^{(1)}_{\alpha j}$ and $\overleftrightarrow{F}^{(2)}_{\alpha j}$ are the first and second moments of these elements. $\overleftrightarrow{M}^{(2)}_{\alpha j}$ is a 3x3 real matrix of all 2nd order moments $(I_{200})_{\alpha j}$, $(I_{110})_{\alpha j}$ ...) of $G_{\alpha j}(\vec{R};t)$. The real and imaginary parts of equation (A.2) yield equations (II.7a) and (II.7b) for $\dot{\vec{P}}_{\alpha j}(t)$ and $\dot{\vec{R}}_{\alpha j}(t)$ respectively.

The equations for the elements of $\overleftrightarrow{A}_{\alpha j}(t)$ are not so easily separable. We can combine (A.1) with (A.3) however to write

$$\int d\vec{R}\,\Big[(\vec{R}-\vec{R}_{\alpha j}(t))^2 - \frac{\overleftrightarrow{M}^{(2)}_{\alpha j}}{(I_{000})_{\alpha j}}\Big]\,|G_{\alpha j}(\vec{R};t)|^2 \qquad (A.4)$$

$$[(\vec{R}-\vec{R}_{\alpha j}(t))\cdot\overleftrightarrow{D}_{\alpha j}(t)\cdot(\vec{R}-\vec{R}_{\alpha j}(t))] + \overleftrightarrow{F}^{(2)}_{\alpha j} - \overleftrightarrow{M}^{(2)}_{\alpha j} F^{(0)}_{\alpha j}/(I_{000})_{\alpha j} = 0$$

where

$$\overleftrightarrow{D}_{\alpha j}(t) = \dot{\overleftrightarrow{A}}_{\alpha j}(t) + \frac{2}{M}\,\overleftrightarrow{A}_{\alpha j}(t)\cdot\overleftrightarrow{A}_{\alpha j}(t) \quad .$$

This can not be reduced to a simple matrix equation for $\overleftrightarrow{D}_{\alpha j}(t)$. However, the matrix of equations (A.4) is symmetric, and three of the equations are redundant. Thus, we solve for $\vec{\lambda}_{\alpha j}$, a vector containing the six non-redundant elements;

$$\vec{\lambda}_{\alpha j} = ((D_{\alpha j}(t))_{xx}; (D_{\alpha j}(t))_{yy}; (D_{\alpha j}(t))_{zz}; 2(D_{\alpha j}(t)_{xy};$$
$$2(D_{\alpha j}(t))_{xz}; 2(D_{\alpha j}(t))_{yz} .$$

Upon integration, and a bit of matrix alegbra, equation (A.4) can be written as

$$\overleftrightarrow{M}^{(4)}_{\alpha j} \cdot \vec{\lambda}_{\alpha j} + \vec{c}_{\alpha j} = 0,$$

where

$$\vec{c}_{\alpha j} = \begin{pmatrix} (F^{(2)}_{\alpha j})_{xx} \\ (F^{(2)}_{\alpha j})_{yy} \\ (F^{(2)}_{\alpha j})_{zz} \\ (F^{(2)}_{\alpha j})_{xy} \\ (F^{(2)}_{\alpha j})_{xz} \\ (F^{(2)}_{\alpha j})_{yz} \end{pmatrix} - \frac{F^{(0)}_{\alpha j}}{(I_{000})_{\alpha j}} \vec{I}^{(2)}_{\alpha j} .$$

$\vec{I}_{\alpha j}$ is a vector of all second order moments of $G_{\alpha j}(\vec{R};t)$;

$$\vec{I}^{(2)}_{\alpha j} = \begin{pmatrix} (I_{200})_{\alpha j} \\ (I_{020})_{\alpha j} \\ (I_{002})_{\alpha j} \\ (I_{110})_{\alpha j} \\ (I_{101})_{\alpha j} \\ (I_{011})_{\alpha j} \end{pmatrix}$$

and

$$\overleftrightarrow{M}^{(4)}_{\alpha j} = \overleftrightarrow{I}^{(4)}_{\alpha j} - \frac{(\vec{I}^{(2)}_{\alpha j})^{+}(\vec{I}^{(2)}_{\alpha j})}{(I_{000})_{\alpha j}} ,$$

where $I^{(4)}_{\alpha j}$ is a real symmetric 6x6 matrix of all fourth order moments; (we drop the subscript αj).

$$\begin{pmatrix} I_{400} & I_{220} & I_{202} & I_{310} & I_{301} & I_{211} \\ I_{220} & I_{040} & I_{022} & I_{130} & I_{121} & I_{031} \\ I_{202} & I_{022} & I_{004} & I_{112} & I_{103} & I_{013} \\ I_{310} & I_{130} & I_{112} & I_{220} & I_{211} & I_{121} \\ I_{301} & I_{121} & I_{103} & I_{211} & I_{202} & I_{112} \\ I_{211} & I_{031} & I_{013} & I_{121} & I_{112} & I_{022} \end{pmatrix}$$

Thus

$$\vec{\lambda}_{\alpha j} = - (\overleftrightarrow{M}^{(4)}_{\alpha j})^{-1} . \vec{c}_{\alpha j} ,$$

and we arrive at matrix equation (II.7c), where

$$\overleftrightarrow{S}_{\alpha j} = - (\overleftrightarrow{M}^{(4)}_{\alpha j})^{-1} \cdot \overleftarrow{c}_{\alpha j}$$

Finally, using the fact that

$$\int d\vec{R} |G_{\alpha j}(\vec{R};t)|^2 (\vec{R}-\vec{R}_{\alpha j}(t)) \cdot \overleftrightarrow{D}_{\alpha j}(t) \cdot (\vec{R}-\vec{R}_{\alpha j}(t)) = \vec{I}^{(2)}_{\alpha j} \cdot \vec{\lambda}_{\alpha j},$$

we can write equation (A.1) as equation (II.7d) for $\dot{\gamma}_{\alpha j}(t)$.

As mentioned in the text, the ability to compute these three dimensional moment and potential integrals analytically is a tremendous advantage of using the Gaussian basis. The moments are straightforward to compute and can be derived from

$$(I_{000})_{\alpha j} = \int d\vec{R}\, e^{-\frac{2}{\hbar}\vec{R}\cdot[\mathrm{Im}(\overleftrightarrow{A}^{(t)}_{\alpha j})]\cdot\vec{R}}\, e^{-\frac{2}{\hbar}\mathrm{Im}(\gamma_{\alpha j}(t))} =$$

$$= e^{-\frac{2}{\hbar}\mathrm{Im}(\gamma_{\alpha j}(t)} \sqrt{\frac{\pi^3\hbar^3}{8\det(\mathrm{Im}(\overleftrightarrow{A}_{\alpha j}(t)))}}$$

All moments can be generated by taking derivatives of $(I_{000})_{\alpha j}$ with respect to the elements of $A_{\alpha j}(t)$. For example

$$(I_{200})_{\alpha j} = -\frac{\hbar}{2} \frac{\partial}{\partial(\overleftrightarrow{A}_{\alpha j}(t))_{xx}} I_{000}$$

$$= \frac{\hbar}{4} (I_{000})_{\alpha j} \frac{\mathrm{Im}(A_{\alpha j}(t)_{yy}\mathrm{Im}(A_{\alpha j}(t))_{zz} - (\mathrm{Im}(A_{\alpha j}(t))_{zy}}{\det(\mathrm{Im}(\overleftrightarrow{A}_{\alpha j}(t)))}$$

All odd order moments are zero.

The potential integrals in $F_{\alpha j}$ can all be written as sums of terms of the form

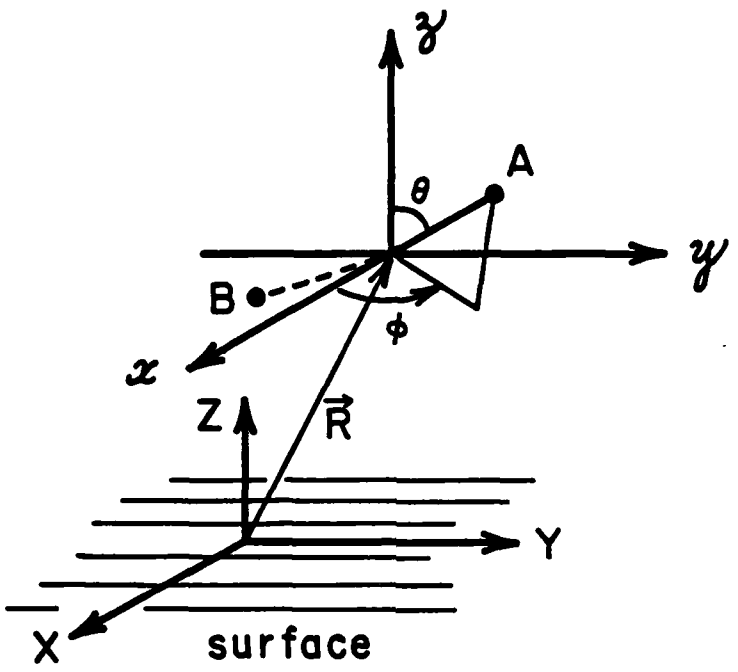
$$c \int d\vec{R}\, (\vec{R}-\vec{R}_{\alpha j}(t))^n\, e^{-\vec{R}\cdot\overleftrightarrow{\Delta}\cdot\vec{R} - \vec{\Gamma}\cdot\vec{R}},$$

where c is some collection of constants, and the wave packet and potential parameters are contained in Δ and $\vec{\Gamma}$. For n = 0, we can

complete the square to find

$$\int d\vec{R}\; e^{-\vec{R}\cdot\overleftrightarrow{\Delta}\cdot\vec{R} - \vec{\Gamma}\cdot\vec{R}} = \sqrt{\frac{\pi^3}{\det\overleftrightarrow{\Delta}}}\; e^{\frac{1}{4}\vec{\Gamma}\cdot(\overleftrightarrow{\Delta})^{-1}\cdot\vec{\Gamma}} .$$

As for the moments of this (n = 1,2) we can simply take derivatives of the above with respect to the elements of $\overleftrightarrow{\Delta}$ and $\vec{\Gamma}$ as was done with $(I_{000})_{\alpha j}$.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